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Stationary source emissions - Determination of the mass concentration of
PCDDs/PCDFs - Part 2: Extraction and clean-up

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentrationen von
PCDDs/PCDFs - Teil 2: Extraktion und Reinigung

Emissions de sources fixes - Détermination de la concentration massique en
PCDDs/PCDFs - Partie 2: Extraction et purification

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Ta slovenski standard je istoveten z: EN 1948-2:1996

ICS:

13.040.40 Ò{ ã ã Á ^] ! ^{ ã } ã ã [ç Stationary source emissions

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ICS 13.040.40

Descriptors: Air, quality, air pollution, gaseous effluents, emission, determination, concentration, PCDD, PCDF, samples, extraction, quality control, purity

English version

Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs — Part 2: Extraction and clean-up

Emissions de sources fixes — Détermination de la concentration massique en PCDDs/PCDFs —
Partie 2: Extraction et purification

Emissionen aus stationären Quellen — Bestimmung der Massenkonzentrationen von PCDDs/PCDFs
Teil 2: Extraktion und Reinigung

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This European Standard was approved by CEN on 1996-12-27. CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart 36, B-1050 Brussels

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 264, Air quality, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 1997, and conflicting national standards shall be withdrawn at the latest by June 1997.

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative annex C, which is an integral part of this standard.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

This European Standard was elaborated by

AENOR (Spain)

AFNOR (France)

BSI (United Kingdom)

DIN (Germany)

DS (Denmark)

NNI (Netherlands)

NSF (Norway)

ON (Austria)

SFS (Finland)

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SNV (Switzerland)

UNI (Italy)

The precision and the performance characteristics were determined in four comparative and validation trials at waste incinerators sponsored by the Commission of the European Communities, the European Free Trade Association and the German Federal Environment Agency.

This European Standard EN 1948-2:1996 consists of:

Part 1. Sampling

Part 2. Extraction and clean-up

Part 3. Identification and quantification

All three parts are necessary for the performance of the dioxin measurements.

The European Standard was developed on the basis of the following national standards or guidelines:

NFX 43-313 : 1991	<i>Air Quality — Stationary Source Emissions — Determination of PCDD/PCDF</i>
Nordic : 1987	<i>Recommended method for dioxin measurements in flue gases from waste incineration, Swedish Environmental Protection Agency</i>
Unichim Method N° 825 : 1989	<i>Stationary source emission measurements</i> <i>Conveyed gas flows</i> <i>Sampling and determination of organic micropollutants</i> — <i>Sampling</i> — <i>PAH determination</i> — <i>PCDD and PCDF determination</i> — <i>PCB determination</i>
VDI 3499 Part 1 : 1990 (Draft)	<i>Emission measurement — Measurement of residual materials — Determination of polychlorinated dibenzodioxins and dibenzofurans in flue and stack gas of incineration and firing plants — Dilution method — Determination in filter dust, potash and slag</i>
VDI 3499 Part 2 : 1993 (Draft)	<i>Emission measurement — Determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) — Filter/condenser method</i>
VDI 3499 Part 3 : 1996 (Draft)	<i>Emission measurement — Determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) — Cooled probe method</i>

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Introduction

Two groups of related chlorinated aromatic dibenzo ethers are known as polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs); they consist of a total of 210 individual substances (congeners): 75 PCDDs and 135 PCDFs.

PCDDs and PCDFs can form in the combustion of organic materials; they also may occur as undesirable by-products in the manufacture or further processing of chlorinated organic chemicals. PCDDs/PCDFs enter the environment via these emission paths and through the use of contaminated materials. In fact, they are universally present in very small concentrations.

The 2,3,7,8-chlorine substituted congeners are toxicologically significant. Toxicologically much less significant than the tetrachlorinated to octachlorinated dibenzodioxins/dibenzofurans are the 74 monochlorinated to trichlorinated dibenzodioxins/dibenzofurans (for toxicity equivalent factors, see annex A of EN 1948-1 : 1996).

Only skilled operators who are trained in handling highly toxic compounds should apply this standard.

1 Scope

The present Part of this standard specifies the extraction and clean-up procedures of the sampled PCDDs/PCDFs. It is an integral part of the complete measurement procedure. The use of the other two Parts EN 1948-1 : 1996 and EN 1948-3 : 1996 describing sampling or identification and quantification, respectively, is necessary for the determination of the PCDDs/PCDFs.

This standard has been designed to measure PCDD/PCDF concentrations at about 0,1 ng I-TEQ/m³ in stationary source emissions.

This standard specifies both method validation and a framework of quality control requirements which have to be fulfilled by any PCDD/PCDF extraction and clean-up methods to be applied. Some methods are described in detail in annex A as examples of proven procedures.

Each of the three sampling methods (Part 1) can be combined with the extraction and clean-up (Part 2) and the identification and quantification (Part 3) to complete the measurement procedure.

During comparison measurements on a municipal waste incinerator at the level of about 0,1 ng I-TEQ/m³ these three methods have been deemed comparable within the expected range of uncertainty. Validation trials were performed on the flue gas of municipal waste incinerators at the level of about 0,1 ng I-TEQ/m³ and a dust loading of from 1 mg/m³ to 15 mg/m³.

In principle it is not possible to evaluate the accuracy (trueness and precision) of emission measurements. Following the validation trials the internal and external variabilities were calculated for the process considered and are given in clause 13 of EN 1948-3 : 1996. These variabilities give an indication of the variabilities which have been observed when using this standard and should be taken into account when expressing results.

The procedure described in the three Parts of standard EN 1948 : 1996 lays down requirements in order to measure the 17 congeners required to calculate the total I-TEQ (see table A.1 of EN 1948-1 : 1996).

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

- | | |
|------------------|---|
| EN 1948-1 : 1996 | <i>Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs — Part 1: Sampling</i> |
| EN 1948-3 : 1996 | <i>Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs — Part 3: Identification and quantification</i> |

A bibliography is shown in annex B (informative).

3 Definitions and abbreviations

3.1 Definitions

For the purposes of this standard, the following definitions apply:

3.1.1 spiking

Addition of $^{13}\text{C}_{12}$ -labelled PCDD/PCDF standards.

3.1.2 isokinetic sampling

Sampling at a rate such that the velocity including the direction of the gas entering the sampling nozzle is the same as that of the gas in the duct at the sampling point. [ISO 9096 : 1992]

3.1.3 operational performance characteristics

Measures which deal with the influence of the physical and chemical environment and maintenance problems, for example; mains voltage, temperature, supply of certain substances, set-up time, period of unattended operation.

3.1.4 statistical performance characteristics

Measures which quantify, for measured values, the possible deviations resulting from the random part of the measuring process; these are, for example, repeatability or instability.

3.1.5 control blank

A sample taken at the plant site in an identical manner to the normal samples including the spiking but without introducing the probe into the flue gas and without introducing air into the sampling train. All the compartments up to and including the last collecting stage are rinsed or extracted in the normal manner.

3.1.6 extraction blank

A blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all the relevant reagents and materials.

3.1.7 sampling standard

$^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDD/PCDF, added before sampling.

3.1.8 extraction standard

$^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDD/PCDF, added before extraction and used for calculation of results.

3.1.9 syringe standard

$^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDD/PCDF, added before injection into the GC.

3.1.10 keeper

High boiling point solvent added to the sampling standard solution.

3.1.11 congener

Any one of the 210 individual PCDDs/PCDFs.

3.1.12 PCDD/PCDF isomers

PCDDs or PCDFs with identical chemical composition but different structure.

3.1.13 pattern

Defined as a chromatographic print of any series of PCDD/PCDF isomers.

3.1.14 profile

Graphic representation of the sums of the isomer concentrations of the PCDDs and the PCDFs.

3.2 Abbreviations

3.2.1 I-TEQ

International toxic equivalent obtained by weighting the mass determined with the corresponding I-TEF. (For detailed description, see annex A of EN 1948-1 : 1996.)

3.2.2 I-TEF

International toxic equivalent factor. (For detailed description, see annex A of EN 1948-1 : 1996.)

3.2.3 GC/MS

Gas chromatography/mass spectrometry.

3.2.4 TCDD

Tetrachlorodibenzo-p-dioxin.

3.2.5 PeCDD

Pentachlorodibenzo-p-dioxin.

3.2.6 HxCDD

Hexachlorodibenzo-p-dioxin.

3.2.7 HpCDD

Heptachlorodibenzo-p-dioxin.

3.2.8 OCDD

Octachlorodibenzo-p-dioxin.

3.2.9 PCDD

Polychlorodibenzo-p-dioxin.

3.2.10 TCDF

Tetrachlorodibenzofuran.

3.2.11 PeCDF

Pentachlorodibenzofuran.

3.2.12 HxCDF

Hexachlorodibenzofuran.

3.2.13 HpCDF

Heptachlorodibenzofuran.

3.2.14 OCDF

Octachlorodibenzofuran.

3.2.15 PCDF

Polychlorodibenzofuran.

3.2.16 PCDDs/PCDFs

Polychlorinated dibenzo-p-dioxins/dibenzofurans.

3.2.17 PTFE

Polytetrafluoroethylene.

4 Principle of the extraction and clean-up procedure

The determination of PCDDs/PCDFs is based on quantification by the isotope-dilution technique using GC/MS. $^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDD/PCDF congeners are added at different stages of the whole method. Losses during extraction and clean-up can be detected and compensated by using these added congeners as internal standards for quantification together with syringe standards which are added just before the GC/MS analysis. However, due to possible differences in the binding and adsorption characteristics of native PCDDs/PCDFs and the added $^{13}\text{C}_{12}$ -labelled congeners, a complete control of the extraction efficiency and compensation of losses during clean-up is not guaranteed. Therefore, in addition the applied methods have to be validated thoroughly. Examples of well-proven extraction and clean-up methods are described in detail in annex A.

The main purpose of the clean-up procedure of the raw sample extract is the removal of sample matrix components, which may overload the separation method, disturb the quantification or otherwise severely impact the performance of the identification and quantification method. Furthermore, an enrichment of the analytes in the final sample extract is achieved. Extraction procedures are normally based on soxhlet extraction of filters and adsorbents, and liquid extraction of the condensate. Sample clean-up is usually carried out by multi-column liquid chromatographic techniques using different adsorbents.

In principle any clean-up method can be used which recovers the analytes in sufficient quantities. Furthermore, the final sample extract shall not affect adversely the performance of the analytical system or the quantification step. However, all applied methods have to be tested thoroughly and have to pass a set of method validation requirements before they can be employed for emission surveillance. In addition, the control of the method performance for each single sample has to be part of the applied quality assurance protocol. This Part of the standard describes a framework of method validation and quality control requirements which have to be fulfilled by any applied method.

In the present Standard the minimum requirements for extraction and clean-up to be met are described as well as examples of operation.

5 Device, materials and $^{13}\text{C}_{12}$ -labelled standards

5.1 Device and materials

See examples of operation in annex A.

5.2 $^{13}\text{C}_{12}$ -labelled standards

The extraction standards (see table 1) shall be added to the different sampling media immediately after arrival of the samples in the laboratory. These $^{13}\text{C}_{12}$ -labelled congeners behave equally to the extracted native PCDDs/PCDFs during clean-up due to their similar chemical and physical properties. Consequently, they are used for quantification.

The quantities of the $^{13}\text{C}_{12}$ -labelled congeners to be added per sample for sampling at the concentration level of 0,1 ng I-TEQ/m³ and 10 m³ sampling volume (dry gas) are given in table 1.

If a considerably higher or lower mass of native PCDDs/PCDFs is expected in the sample, the masses of the $^{13}\text{C}_{12}$ -labelled standards to be added shall be adapted accordingly.

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Table 1. $^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDD s/PCDFs congeners to be added to the sample at different stages of the procedure for 0,1 ng I-TEQ/m³ and 10 m³ sampling volume (dry gas)

	Total amount in pg added before:		
	Sampling (sampling standard)	Extraction (extraction standard)	GC Injection (syringe standard) (recovery)
Solution: Total volume in μl : (e.g. toluene, n-nonane)	100	100	25
Congeners added			
$^{13}\text{C}_{12}$ -2,3,7,8-TCDF		400	
$^{13}\text{C}_{12}$ -1,2,3,4-TCDD			400
$^{13}\text{C}_{12}$ -2,3,7,8-TCDD		400	
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF	400		
$^{13}\text{C}_{12}$ -2,3,4,7,8-PeCDF		400	
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD		400	
$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF		400	
$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDF		400	
$^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDF	400		
$^{13}\text{C}_{12}$ -2,3,4,6,7,8-HxCDF		400	
$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDD		400	
$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD		400	
$^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD			400
$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF		800	
$^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF	800		
$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD		800	
$^{13}\text{C}_{12}$ -OCDF		800	
$^{13}\text{C}_{12}$ -OCDD		800	

6 Method validation and quality control requirements

6.1 Use of $^{13}\text{C}_{12}$ -labelled standards

$^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDDs/PCDFs are added before sampling (sampling standards), before extraction (extraction standards) and just before the GC injection (syringe standards). The syringe standards are assumed to be transferred to the analytical system without any loss and allow to determine the recoveries (or losses) of the congeners added at earlier stages.

Sampling standards are added to the sampling device before starting sampling. $^{13}\text{C}_{12}$ -labelled congeners introduced at this stage might not be exposed to completely the same mechanisms of losses as the native PCDDs/PCDFs collected during the sampling period. First, the labelled congeners are exposed to the gas flow during the entire sampling time while the native PCDDs/PCDFs are present only half the time on average. Second, a significant fraction of the sampled native PCDDs/PCDFs are bound to particles and, therefore, they may have different susceptibilities to reactions and mechanisms which might lead to losses. Consequently, as different studies have shown, $^{13}\text{C}_{12}$ -labelled congeners added prior to sampling might be subject to loss mechanisms. Their use as internal standards for quantification may lead to an overestimation of the found concentrations. Therefore, the only purpose of the isotope labelled standards added before sampling (see table 1) is to identify anomalies during sampling. They are not used for quantification.

6.2 Sample pretreatment

The efficiency of all applied extraction methods shall be documented as part of the method description. It shall be measured regularly and corrective action taken if the extraction efficiency falls below the acceptable requirements given below. The following validation criterion shall be fulfilled for all parts of the sampling device that may contain a part of the sample such as (where applicable) filters, ab/adsorbents, condensate, vessels and surfaces of the sampling device.

The extract of a repeated extraction procedure shall not contain more than 5 % of the amount of any individual native congener compared with the first extraction. For the second extraction the addition of $^{13}\text{C}_{12}$ -labelled extraction standards is repeated.

Furthermore, the efficiency of the extraction method shall be controlled for each individual sample by adding a set of $^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted congeners to the sampling train compartments prior to extraction.

6.3 Clean-up

6.3.1 Method validation

Sample clean-up is dependent on the type of sample matrix which shall be removed. Therefore, a single well-defined clean-up procedure shall be applied to all sample matrices without preliminary check.

Therefore, the following method validation requirements have been set up which allow to verify the overall performance of the clean-up method in a sample-independent manner. The following requirements shall be fulfilled by any clean-up procedure which is employed.

- The isomer pattern and congener profile of a well characterized sample extract containing all PCDD/PCDF congeners (e.g. a fly ash extract) shall not be altered by the applied clean-up procedure. Area response changes relative to the most abundant signal of each homologue series should not exceed 20 %. Furthermore, differences between the sum responses of the PCDDs/PCDFs congener group should not exceed 20 %.
- The recovery rate for each of the individual congeners of the 2,3,7,8-chlorine substituted PCDDs/PCDFs congeners added before extraction shall be at least 50 % and should not exceed 115 %.

These performance tests shall be repeated after any changes of the clean-up procedure.

In addition, the performance of the clean-up method shall be controlled for each individual sample by calculating the recovery rates of the $^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted congeners added to the sample prior to extraction.

6.3.2 Minimum requirements for measurements

The recovery rate of each individual 2,3,7,8-chlorine substituted PCDD/PCDF of the extraction standards shall be within:

- 50 % to 130 % for the tetra- to hexa-chlorinated congeners;
- 40 % to 130 % for the hepta- and octa-chlorinated congeners.

If the above ranges are exceeded, then provided the sum of the contributions to the total I-TEQ from all the congeners with recoveries not within these ranges does not exceed 10 %, the acceptable ranges shall be:

- 30 % to 150 % for the tetra- to hexa-chlorinated congeners;
- 20 % to 150 % for the hepta- and octa-chlorinated congeners.

7 Sample pretreatment and extraction

7.1 Addition of extraction standards

The $^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted congeners listed in table 1 shall be added before extraction. The extraction standards shall be split and distributed proportionally to the sampling train compartments which are known to contain more than 20 % of the total sample amount. If one collection medium is suspected to contain more than 75 % of the total I-TEQ, the whole extraction standard solution should be added to this Part.

7.2 Sample storage

All sampling media and parts of the sampling train which contain PCDDs/PCDFs shall be stored in the dark and at sub-ambient temperature ($< 4^{\circ}\text{C}$) latest 24 h after sampling. The use of screw-caps with PTFE-lined seals is recommended to avoid contamination. Aluminium-lined cardboard seals may contain PCDDs/PCDFs.

7.3 Extraction

The extraction procedure is carried out using the following materials and techniques. Detailed descriptions of some procedures are given in annex A. Other methods can also be used but shall be of proven equal performance as the techniques below.

- a) Particle collecting media (glass fibre filters, thimbles, glass wool etc.): Soxhlet extraction with toluene.
- b) Solid adsorbents (Polyurethane foam, XAD-2, Porapak PS): Soxhlet extraction for 20 h with toluene. (Water shall be removed, e.g. via a Dean-Stark water separator or by sodium sulfate.)
- c) Florisil: Elution with dichloromethane after placing the material in a glass column.
- d) Aqueous liquids (condensate and bubbler/impinger solution): Liquid/liquid extraction with toluene or dichloromethane. The water/toluene volume ratio should not be greater than 20:1. Three consecutive extractions shall be carried out.
- e) Inner surfaces of tubes, vessels or other parts of the sampling device being in contact with the sample: Rinsing with a water-miscible solvent (acetone, methanol) followed by toluene. Reflux boiling with toluene is an alternative for the second step. Pretreatment of sampled particles with hydrochloric acid shall be part of any extraction procedure (examples of procedures are given in annex A).
- f) When sampling with flow division is performed, the filter part and the condenser/adsorber part may be analysed separately. The measured concentrations shall be added at the final stage of calculation. Alternatively an aliquot of the filter extract, corresponding to the proportion of side stream to main stream gas volume, is combined for analysis with the condenser/adsorber part. In this case, the quantity of extraction standard solution added to the filter is increased in proportion to the ratio of main stream to side stream gas volume.
- g) If coke or activated carbon is used in the gas cleaning system of the incinerator suitable methods, including freeze drying or Dean-Stark extraction or addition of water miscible solvents to the extraction medium, shall be taken to remove water. Attention shall be paid to the method validation of this step.

After extraction, the organic solvents containing water shall be dried before the concentration procedure. After combination of all extraction and rinsing solutions any volume reduction shall be carried out carefully to avoid evaporation losses of PCDDs/PCDFs. In case evaporation to nearly dryness is necessary, the use of a small amount (e.g. 50 μl) of a keeper (usually a high-boiling solvent such as tetradecane) is strongly recommended.

7.4 Clean-up

Clean-up methods shall prepare the sample extract in an appropriate manner for the subsequent quantitative determination (see also 6.3). Clean-up procedures have to concentrate PCDDs/PCDFs in the extracts and to remove interfering matrix components present in the raw extract.

Proven clean-up procedures shall be used containing normally two or more of the following techniques which can be combined in different orders. A detailed description of some of the procedures is given in annex A. Other methods can also be used but shall be of proven equal performance as the techniques described below.

a) Gel permeation chromatography

The interesting molecular weight range for PCDDs/PCDFs of 200 g/mol to 500 g/mol can be isolated from larger molecules and polymers which might overload other clean-up methods.

b) Multilayer column liquid chromatography using silica with different activity grades and surface modifications

Compounds with different chemical properties than PCDDs/PCDFs can be removed. A direct treatment of the sample extract with sulfuric acid shall be carried out very carefully to avoid losses of PCDDs/PCDFs on the formed carboniferous surfaces.

c) Column adsorption chromatography using activated carbon

Planar PCDD/PCDF molecules are separated from other interfering non-planar molecules.

d) Column liquid chromatography on alumina of different activity grade and acidity/basicity

Interfering compounds with small differences in polarity or structure compared to PCDDs/PCDFs can be removed.